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*Density, Vapor Pressure, and Viscosity of Solutions
of Hydrazine Mononitrate in Hydrazine*

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ABSTRACT

The density, vapor pressure, and viscosity are reported for two concentrations of hydrazine mononitrate dissolved in anhydrous hydrazine, and for these solutions with approximately 1% of added water. The preparation of the solutions and the techniques used to measure these values are described.

I. INTRODUCTION

The measurement of density, vapor pressure, and viscosity for solutions of hydrazine mononitrate in hydrazine is of interest because of the possible use of this mixture as a rocket fuel. The stability of the mixture is comparable to that of hydrazine, but its

performance is decidedly higher. These density, vapor pressure, and viscosity measurements were made on two concentrations of hydrazine mononitrate in anhydrous hydrazine, and on the same solutions with 1% of added water.

II. PREPARATION OF ANHYDROUS HYDRAZINE

The anhydrous hydrazine was prepared from commercial hydrazine assaying 98.50% hydrazine and containing 0.51% aniline. Water was removed from hydrazine by the addition of barium oxide which reacts chemically with water to give barium hydroxide.¹

Figure 1 shows the apparatus used to prepare the anhydrous hydrazine. (Details of the procedure followed were based on a private communication from Dr. Hans Bock of Munich University.)

The apparatus was evacuated through the tubulation on the weighed 500-cc flask. A liquid nitrogen trap equipped with a stopcock was located between the apparatus and the vacuum pump. To remove water more rapidly from the glass surfaces, the apparatus was lightly flamed.

After a half hour of pumping, the apparatus was isolated from the vacuum system. Air, dried by passage through a drying tube filled with Anhydron, was admitted into the apparatus via the stopcock on the 1-liter flask.

¹Clark, Charles C., "Hydrazine," Matheson Chemical Corporation, Baltimore, Maryland, 1953, pp. 2-3.

One hundred grams of barium oxide were placed in the 1-liter flask. The apparatus was again evacuated and, with the barium oxide heated to 150°C using a heating mantle, pumping was continued for one hour.

After cooling the barium oxide to ambient temperature, dry air was admitted into the apparatus and then 500 ml of commercial hydrazine were quickly added to the 1-liter flask. The apparatus was closed, the hydrazine frozen with dry-ice, and the apparatus evacuated to remove the air. In order to remove the air dissolved in the hydrazine, the apparatus was isolated from the vacuum system, the hydrazine thawed, magnetically stirred, refrozen, and the apparatus again pumped.

After pumping for approximately half an hour, the apparatus was again isolated from the vacuum system, and the hydrazine thawed then magnetically stirred in contact with the barium oxide for one hour at ambient temperature.

The hydrazine was frozen, and the apparatus re-pumped once more. The apparatus was then isolated from the vacuum system, the dry-ice bath transferred to the 500-cc flask, the hydrazine thawed, and the distillation process initiated.

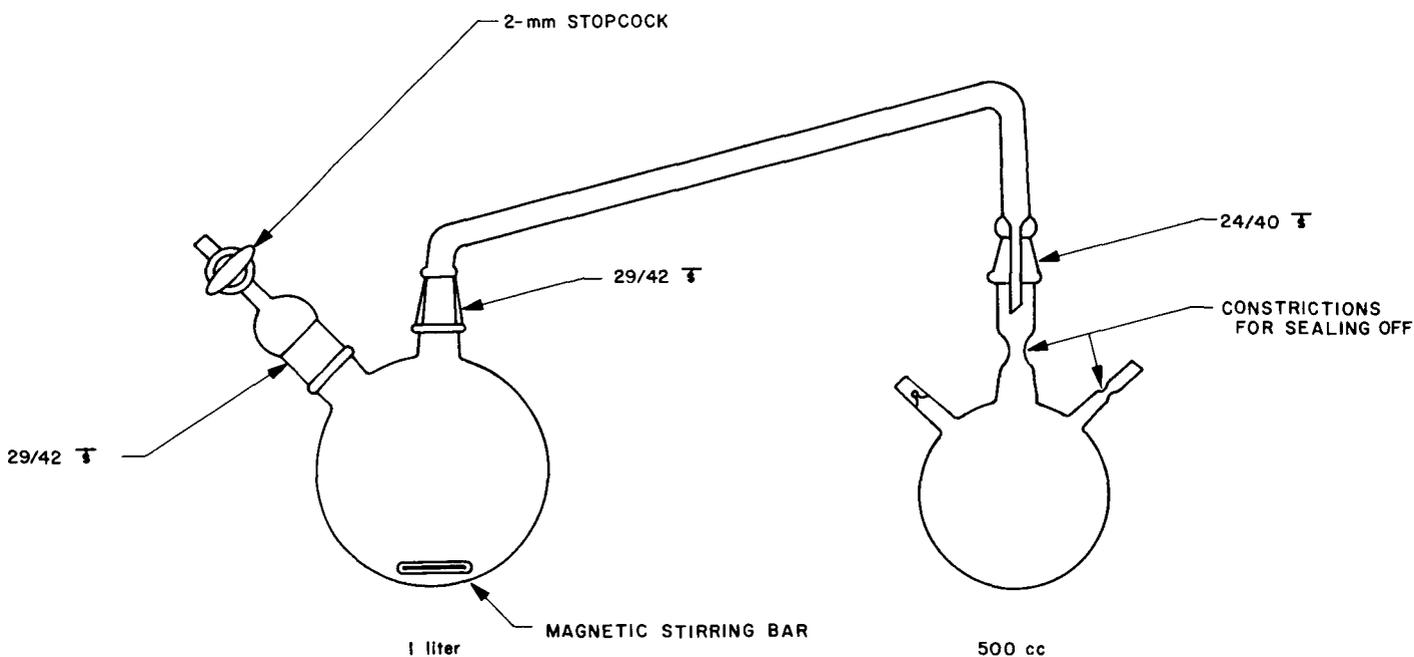


Fig. 1. Apparatus for preparing anhydrous hydrazine

When about 300 ml of hydrazine had been distilled, the hydrazine in both flasks was frozen, the apparatus pumped for about ten minutes and then the 500-cc flask sealed off with a torch at the constrictions, thus sealing

the distilled, anhydrous hydrazine under vacuum in the flask. By reweighing the flask with the sealed-off joint and the tubulation, the weight of distilled hydrazine in the flask can be determined.

III. PREPARATION OF SOLUTION OF HYDRAZINE MONONITRATE IN HYDRAZINE

The hydrazine solutions of hydrazine mononitrate were prepared in the apparatus shown in Fig. 2.

The method of preparation consisted in adding small portions of dried ammonium nitrate to the anhydrous hydrazine and pumping off the evolved ammonia. The equation for this preparation is



From the weight of hydrazine collected, the amount of ammonium nitrate needed to prepare the desired concentrations of hydrazine mononitrate in the hydrazine was calculated. The calculated amount of ammonium nitrate was weighed and then transferred into the ammonium nitrate holder of the apparatus of Fig. 2.

The apparatus was evacuated and the glassware flamed lightly to remove moisture.

With the apparatus isolated from the vacuum system, the break-seal on the flask of anhydrous hydrazine was broken and the other flask cooled with dry-ice. Upon completion of the anhydrous hydrazine distillation, the empty flask was removed with a torch at the seal-off constriction located above the 29/42 joint.

The dewar-type trap above the flask was cooled with dry-ice, and the unit was connected to the vacuum system. Ammonium nitrate in small portions was shaken down into the thawed but cold hydrazine. The evolved NH_3 was pumped out—hydrazine loss being prevented by the dry-ice trap. This preparation was endothermic.

When the ammonium nitrate had been shaken down as completely as possible, the flask was tilted back and forth to wash out any ammonium nitrate still left in the holder.

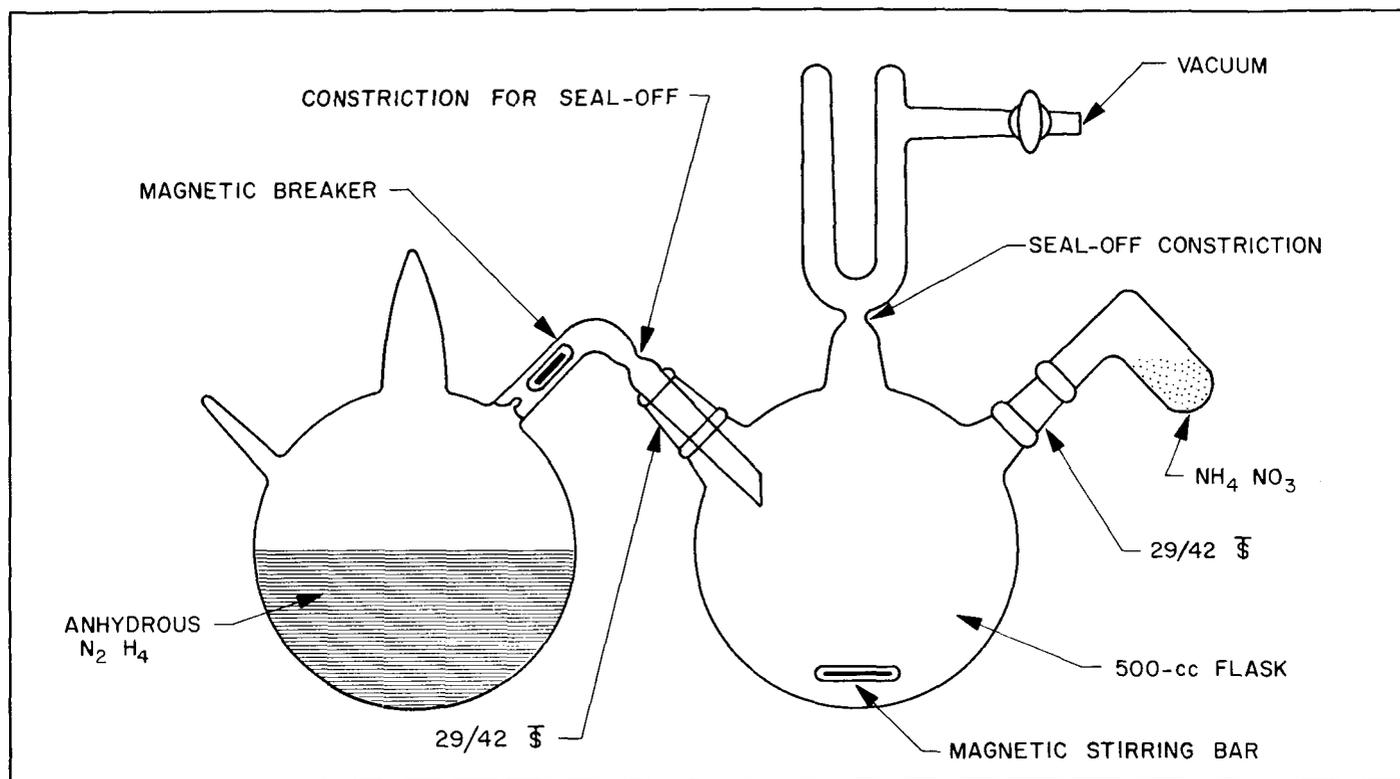


Fig. 2. Apparatus for preparing anhydrous solutions of $N_2H_4 \cdot HNO_3$ in N_2H_4

To remove the ammonia as completely as possible, the solution was stirred for a half hour while pumping.

The stopcock on the dewar-trap was closed, the dry-ice in the trap removed, and the frozen hydrazine thawed and allowed to drip back into the flask. In order to be certain that any hydrazine mononitrate present in the region of the seal-off constriction was completely removed, liquid nitrogen was put into the dewar-trap, then time allowed for a considerable quantity of hydrazine to distill and collect in the trap. Next the trap was warmed and the hydrazine again thawed and allowed to drip back into the flask, thereby thoroughly washing the glass in the region of the seal-off constriction.

The contents of the flask were frozen and the flask sealed off with a torch at the constriction. The thawed solution was swirled around in the flask to mix the contents, and then placed in a dry box.

To minimize contact between Apiezon grease and hydrazine, the stopcocks were lubricated sparingly, and grease was applied only to lower portions of the ground

joints so that the grease in mated joints did not completely cover the ground surfaces.

The mixtures containing water were prepared by weighing out the anhydrous solutions and then adding the required quantity of water to give a 1% water content. Table 1 lists the composition of the prepared solutions. The aniline content in the anhydrous hydrazine prepared was determined spectrometrically, and the rest of the composition calculated from the weights of materials used. The calculated composition was verified by chemical analysis.

Table 1. Composition of solutions of hydrazine mononitrate dissolved in hydrazine*

Solution	% H_2O	% N_2H_4	% $N_2H_4 \cdot HNO_3$	% $C_6H_5NH_2$
1	0.00	82.04	17.62	0.34
2	0.00	69.74	29.97	0.29
3	1.00	81.22	17.44	0.34
4	0.97	69.06	29.68	0.29

*Percent aniline was determined by a spectrometric method and the remaining composition calculated from additions made and the assumption that the hydrazine prepared was anhydrous.

IV. DETERMINATION OF DENSITY

Density measurements were made twice at 0°C, 20°C, 40°C, and 60°C. A specially built pycnometer requiring about 25-cc volume of liquid, having a calibrated stem with subdivisions of 0.01 cc, and read by estimation to

0.001 cc was used. The weighed pycnometer was loaded in the dry box, reweighed and then placed in water baths maintained at the required temperatures. Figures 3 and 4 show the densities of the prepared solutions.

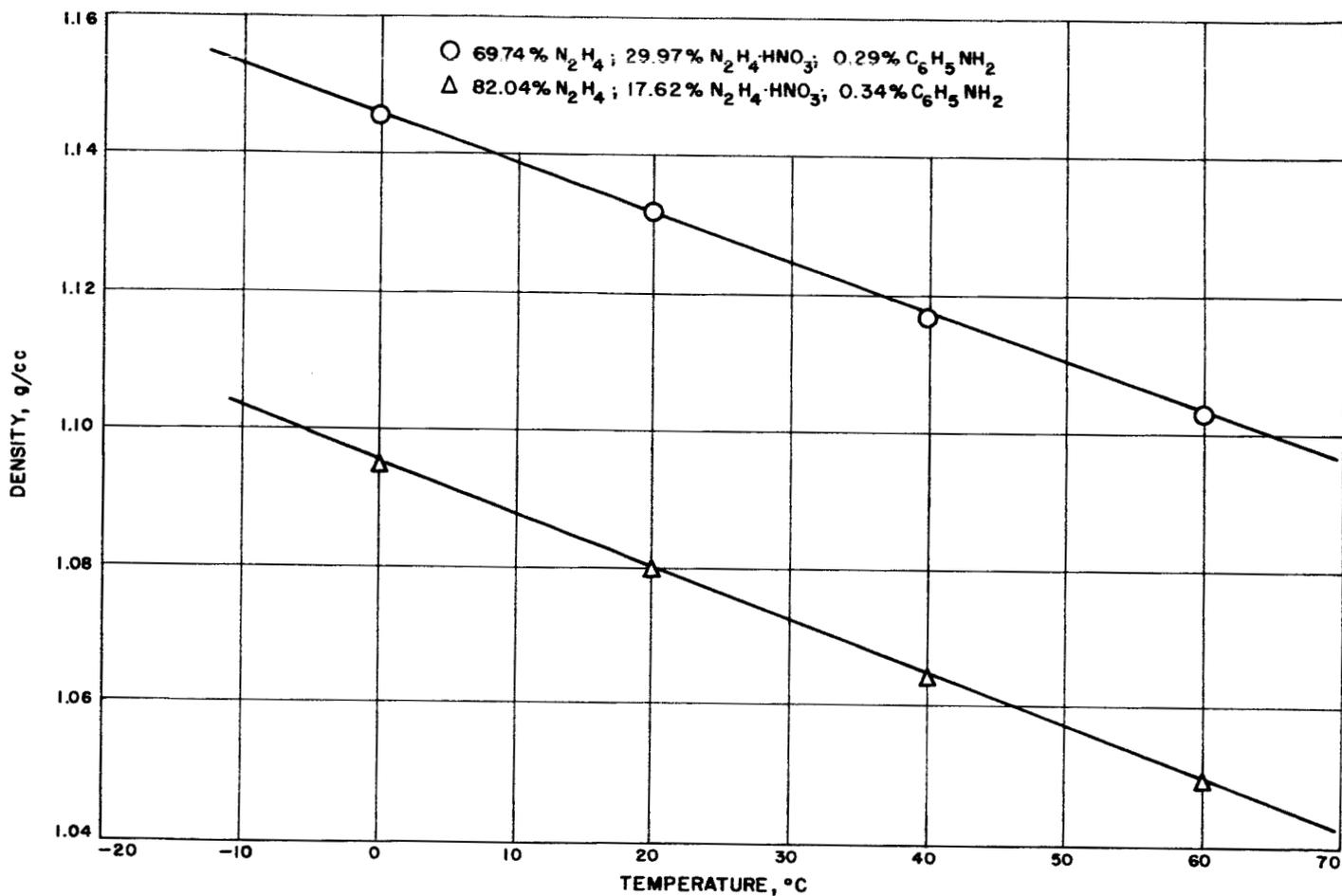


Fig. 3. Density vs. temperature, for anhydrous solutions

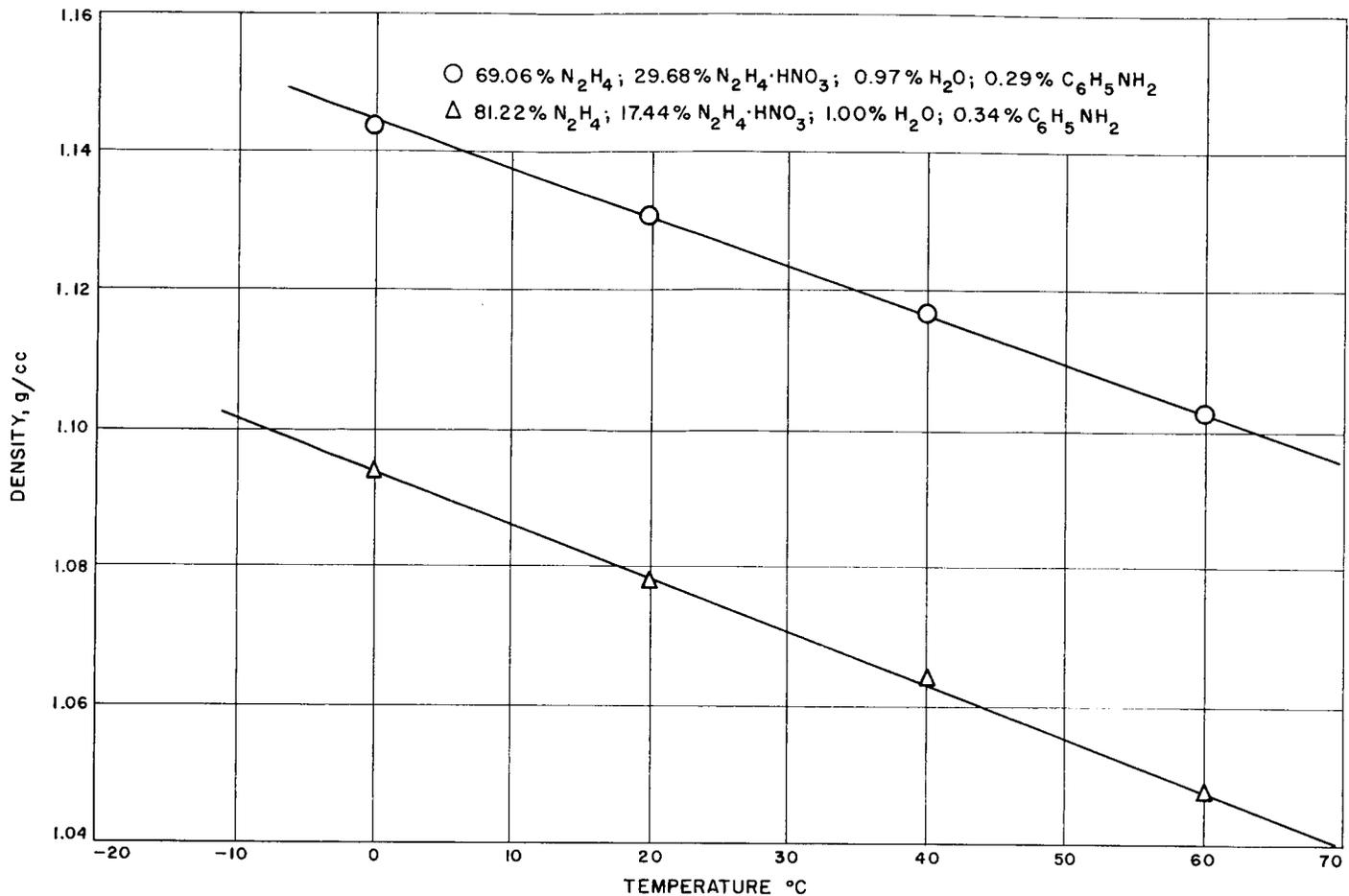


Fig. 4. Density vs. temperature, for solutions containing 1% H_2O

V. VAPOR PRESSURE MEASUREMENTS

In order to remove slight traces of NH_3 which might remain in the prepared solutions, some of the sample was placed in the thoroughly dried apparatus of Fig. 5 through the 19/38 joint. The unit was connected to a high vacuum system. The trap on the right hand side was immersed in a dry-ice bath and the stopcock then carefully opened to the vacuum. Evacuation continued until at last half the liquid had distilled over. To prevent freezing, the solution container was kept in tap water, and the solution was stirred to facilitate removal of NH_3 .

Next the stopcock on the unit was turned off, the unit removed from the vacuum system, and when the hydrazine in the trap had thawed, the unit was rotated back and forth to thoroughly mix the contents. In the dry box, the degassed solution was introduced into the vapor pressure apparatus of Fig. 6. Then this unit was attached to the high vacuum system.

With the solution in the sample holder frozen by dry-ice, the magnetically operated valve was lifted, the stop-

cock opened, and the apparatus evacuated. Then the stopcock and magnetic valve were closed, and the solution was allowed to thaw and was stirred to help remove dissolved air. The solution was refrozen and the apparatus again pumped down. This procedure was repeated several times.

Once the solution and apparatus were pumped air-free, the stopcock and magnetic valve were closed, the

mercury level raised about three fourths of the way up into the manometer, and the solution thawed.

The apparatus was then placed into the appropriate water bath and immersed to a little above the mercury valve. This arrangement made certain that all parts of the solution and its vapor were at the same temperature and, further, that the mercury vapor pressure in the two manometer legs was identical and therefore cancelled out. Figures 7 and 8 show the vapor pressure data.

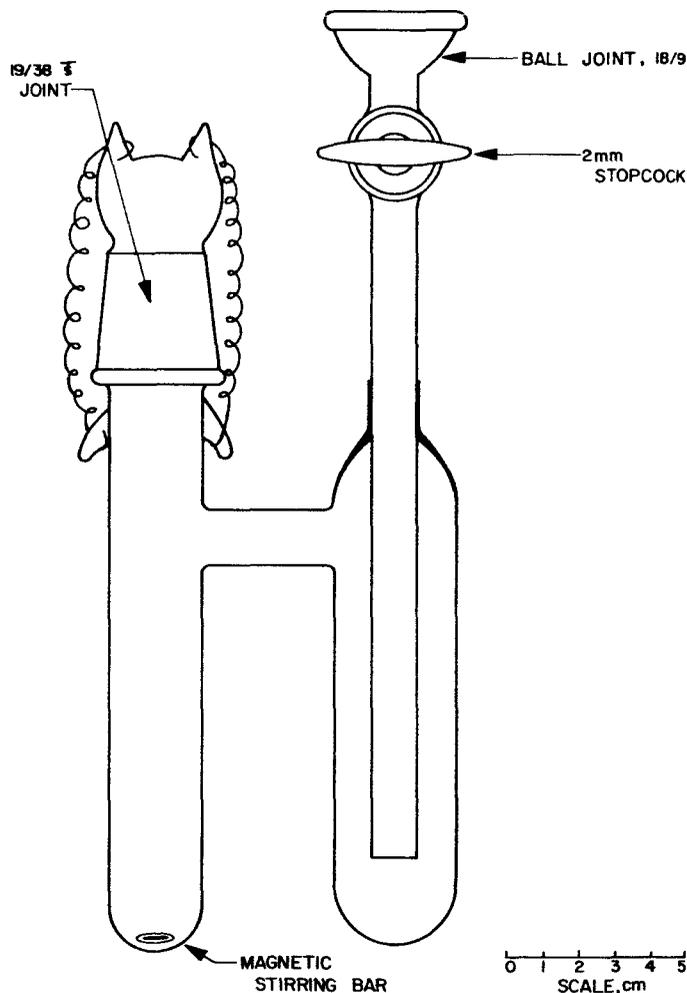


Fig. 5. Apparatus for removing last traces of NH_3 from solutions used for vapor pressure measurements

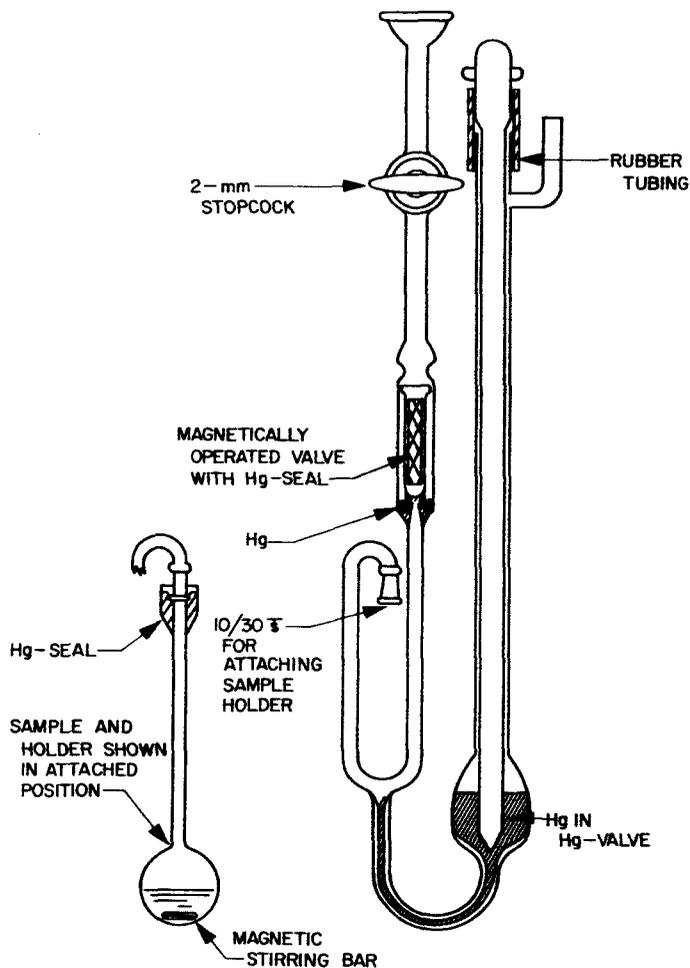


Fig. 6. Vapor pressure apparatus

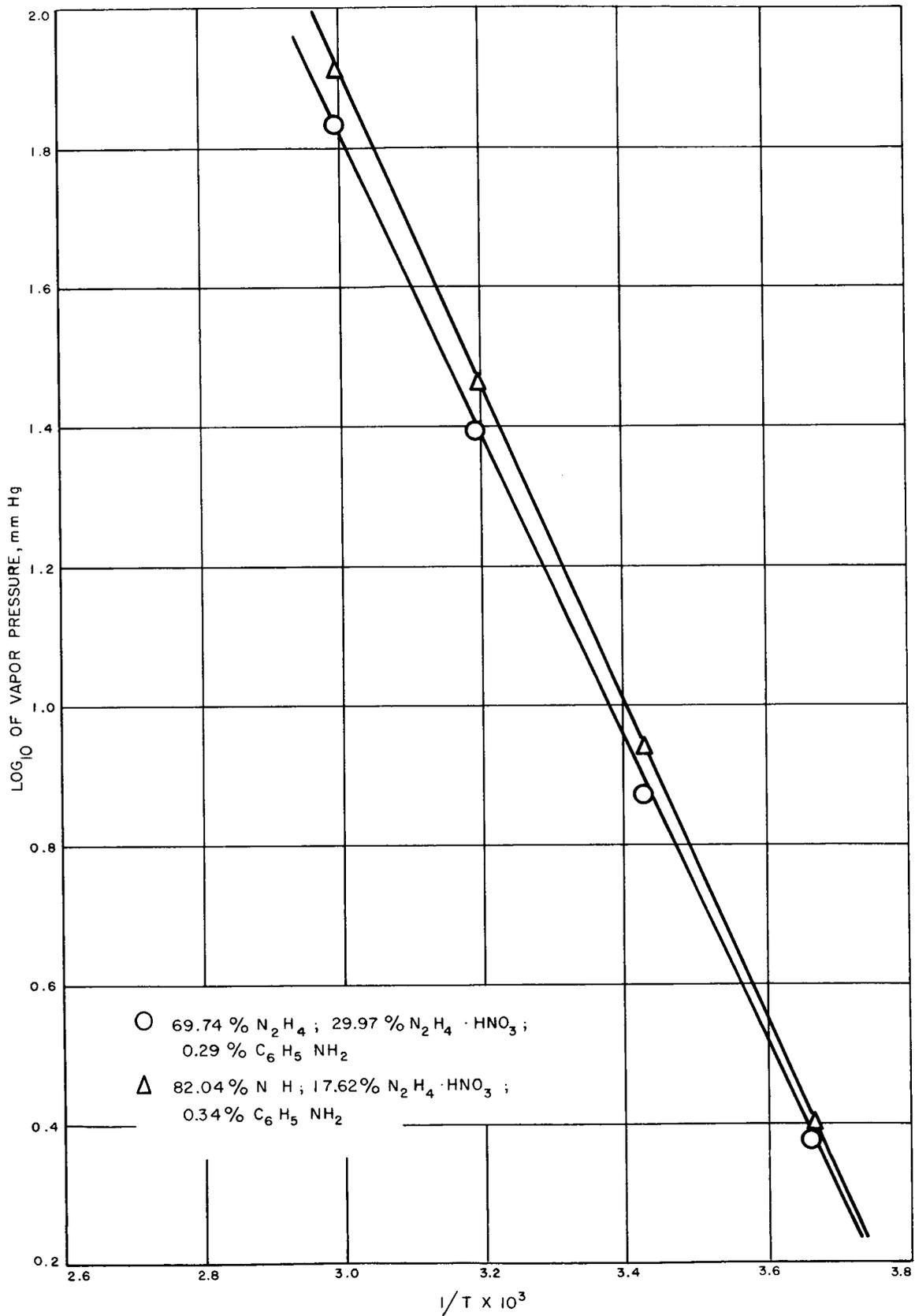


Fig. 7. Logarithm of vapor pressure vs. reciprocal of absolute temperature, for anhydrous solutions

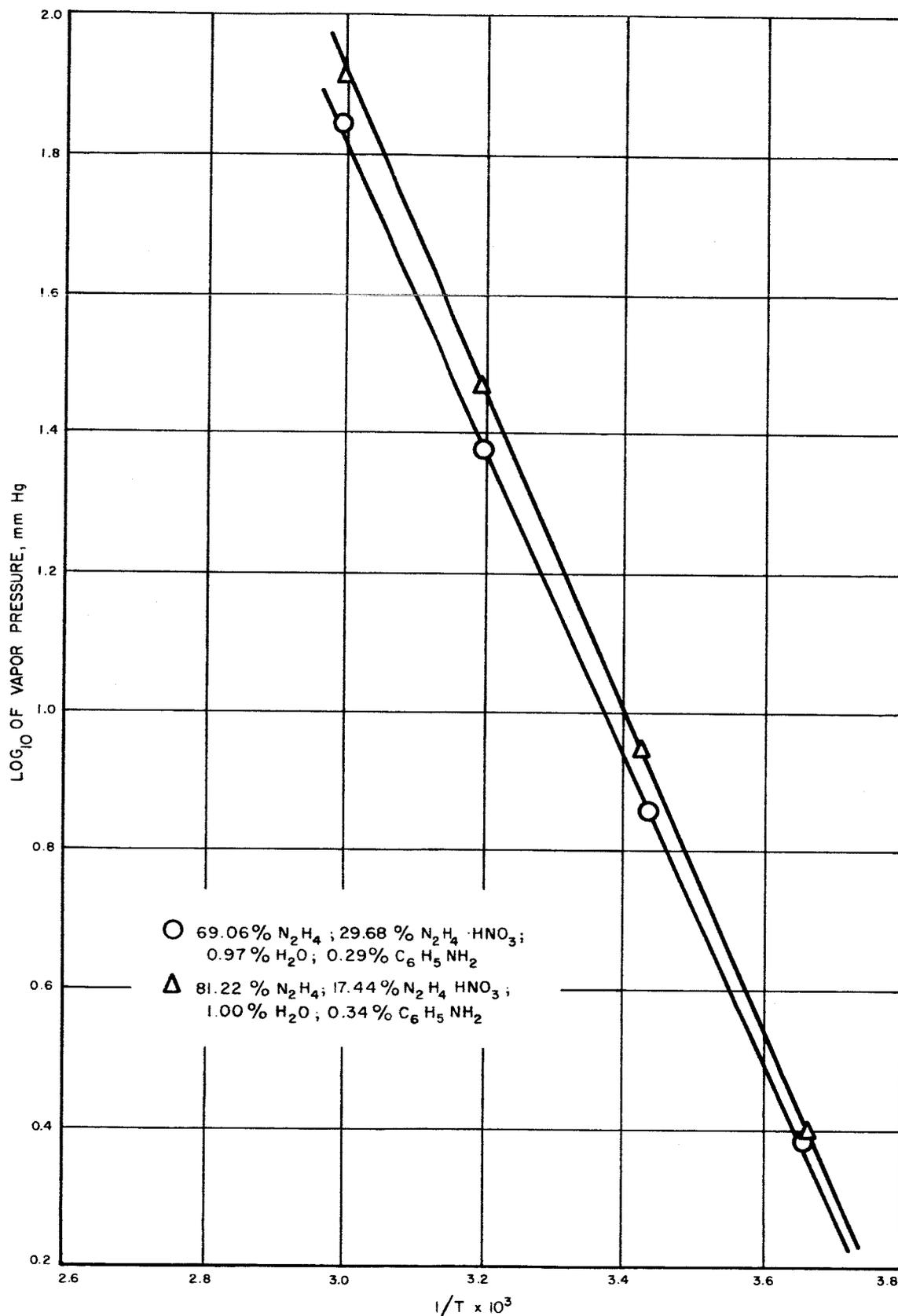


Fig. 8. Logarithm of vapor pressure vs. reciprocal of absolute temperature, for solutions containing 1% H_2O

VI. VISCOSITY MEASUREMENTS

The viscosity measurements were made twice using Cannon-Zhukov viscosimeters fitted with ground joints and caps which seal the viscosimeter contents against

evaporation or moisture pick-up. The results of these viscosity measurements are illustrated in the graphs of Figs. 9 and 10.

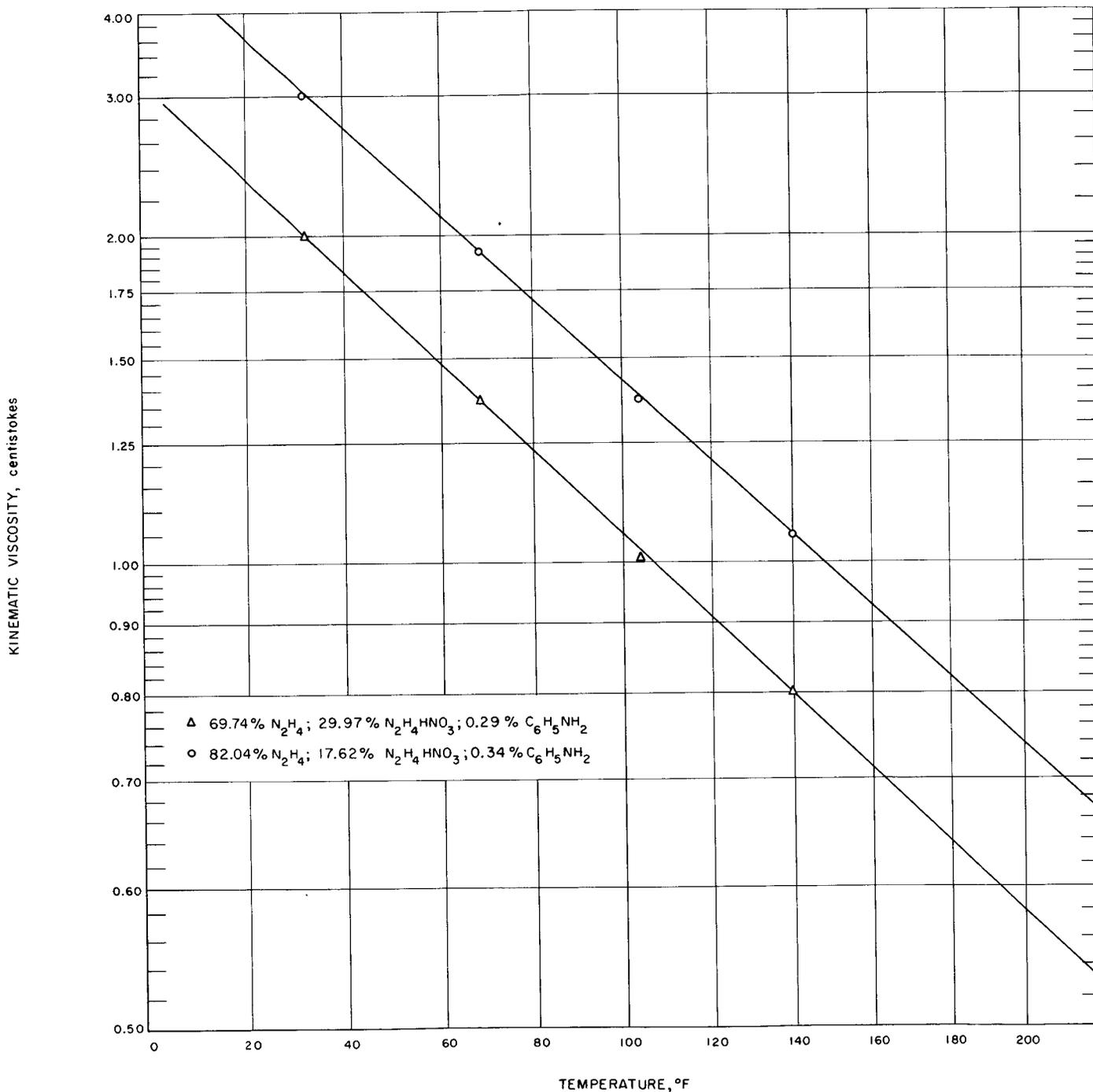


Fig. 9. Kinematic viscosity vs. temperature, °F, for anhydrous solutions

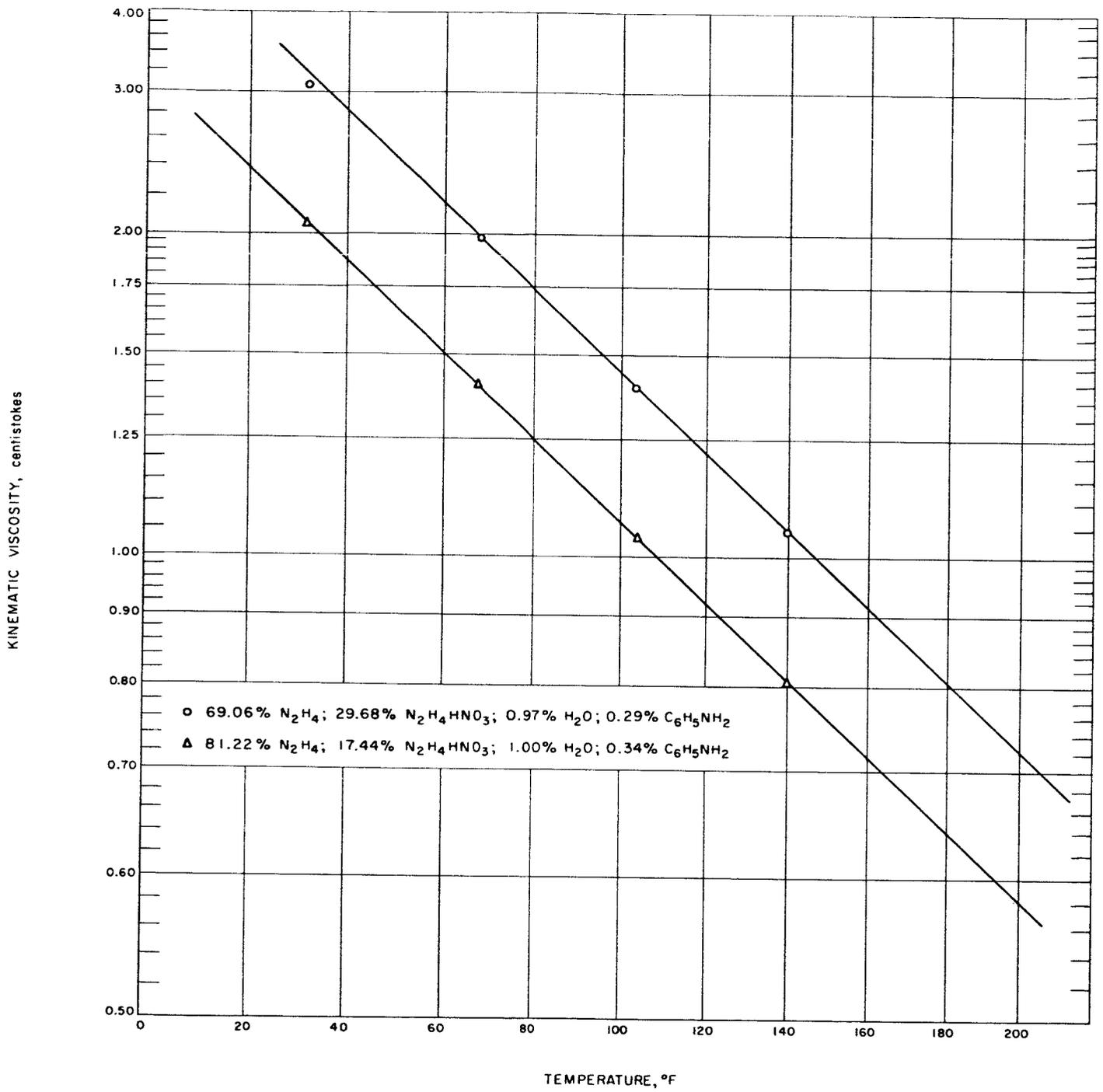


Fig. 10. Kinematic viscosity vs. temperature, °F, for solutions containing 1% H₂O

VII. DISCUSSION

Examination of the data presented shows that the 1% water had essentially no effect on the physical properties measured. In order to detect any possible decomposition of the solutions, the measurements were

made successively in baths of increasing temperature and then returned to the 0°C bath for a recheck. In no case did this final check reveal any evidence of decomposition.